(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 055 016**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 81305175.2

(22) Date of filing: 30.10.81

(51) Int. Cl.³: H 01 M 8/12, H 01 M 8/24, H 01 M 2/20

(30) Priority: 22.12.80 US 219204

(43) Date of publication of application: 30.06.82 Bulletin 82/26

(84) Designated Contracting States: CH DE FR GB IT LI NL SE

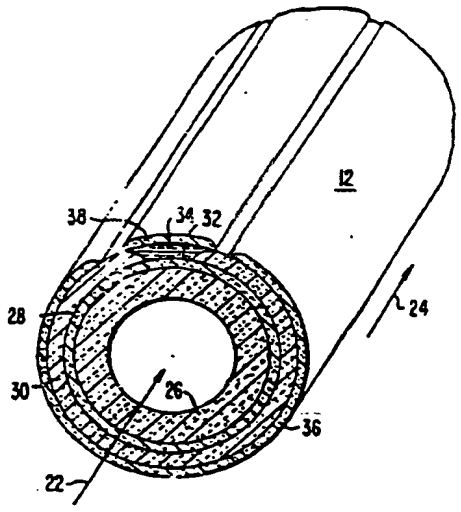
(71) Applicant: WESTINGHOUSE ELECTRIC CORPORATION, Westinghouse Building Gateway Center, Pittsburgh Pennsylvania 15222 (US)

(72) Inventor: Isenberg, Otto Arnold, 327 Woodside Road, Pittsburgh Pennsylvania (US)

(74) Representative: van Berlyn, Ronald Gilbert, 23, Centre Heights, London, NW3 6JG (GB)

(54) High temperature solid electrolyte fuel cell configurations.

(57) High temperature fuel cell configurations and interconnections including annular cells (12) having a solid electrolyte (30) sandwiched between thin film electrodes (28, 36). The cells (12) are electrically interconnected along an elongated axial outer surface through an electrically conductive interconnect (34, 40). With this arrangement, ohmic losses are small since the current is directed from one cell to another through a short path which is normal to the annular surface. Another advantage is an increased reliability since electrical connection is through an elongated surface spanning the length of the cell and hence localized failure will not defeat current transfer.



EP 0 055 016 A1

ACTORUM AG

HIGH TEMPERATURE SOLID ELECTROLYTE FUEL CELL CONFIGURATIONS

This invention relates to fuel cell configurations and more particularly to electrical and structural arrangements of a plurality of such solid electrolyte fuel cells.

High temperature solid electrolyte fuel cells utilizing a natural or synthetic fuel gas such as those containing hydrogen, carbon monoxide, methane, and an oxidant such as oxygen or air, are known. Such cells or stacks of cells operate above 700°C to directly convert chemical energy of the fuel into direct current electrical energy by electrochemical combustion. A typical cell, for example, reacts hydrogen fuel with oxygen from air to produce electrical energy, water vapor and heat.

Each single cell, however, provides a rather small open circuit voltage, on the order of one volt. Accordingly, plural cells are typically connected in series in order to generate a higher voltage output. Various configurations for these connections are known, such as flat plate or generally tubular arrangements. However, such interconnections have given rise to concerns which are difficult to solve. For example, such cells utilize oxide air electrodes which present high lateral ohmic losses, so that the individual cell size must be small with respect to the direction of current flow. Additionally, multiple ceramic and metallic materials are often integrated, presenting differential thermal expan-

sion and materials compatibility concerns. To minimize such concerns, particularly the ohmic losses, the art has utilized small individual band-shaped cells, on the order of one to two centimeters in length, interconnected by good electrical conductors such as noble metals as well as non-noble metals in combination with oxide conductors. Such designs, however, do not alleviate materials compatibility concerns and require a substantial number of fabrication steps to provide an integrated electrical generator of any substantial size. Additionally, the large number of small components, layers, interconnections, and fabrication steps required in such designs raises substantial concerns regarding long-term reliability.

An example of such tubular "band" designs is provided in U.S. Patent No. 3,525,646, which discloses a large plurality of small individual cells arranged along the circumference of a porous support tube. Each individual cell is small, and is electrically interconnected in series to the axially next cell along the tube by a conductor. A large plurality of cells, layers and conductive current collectors are required to achieve a substantial voltage. Preferably, the various layers are deposited on the support tube by plasma or flame spray methods. In addition to the concerns discussed above, such band type systems are susceptible to failure in any one cell or interconnect which defeats electrical interconnection for the entire series connected grouping of cells.

Another fuel cell arrangement is described in German Offenlegungsschrift No. 2,614,728, which, in an effort to obtain high power densities with the fewest possible components, forms scalloped plate type supporting bodies into a plurality of parallel channels. The channels, in conjunction with semicircular electrodes deposited therein, form fuel cells extending the length of the support bodies. The cells are interconnected through abutting radial lips and additional components. This arrangement suffers limitations similar to the deficien-

cies of the band designs, requiring multiple internal unaccessible connectors, and additionally depends upon the supporting plates for structural integrity. This limits the ability to electrically interconnect the cells in desireable manners, since direct contact with the cell is difficult. Additionally, the air oxidant must diffuse through the relatively thick support plates prior to gaining access to the air electrode.

It is desirable to provide a high temperature solid electrolyte fuel cell arrangement which alleviates the concerns of present designs and increases reliability.

This invention provides high temperature solid electrolyte fuel cell configurations and cell arrangements which substantially enhance reliability and alleviate many of the prior art deficiencies such as high ohmic losses, thermal expansion and other materials compatibility concerns.

More specifically, the invention resides in a high-temperature, solid electrolyte electrochemical cell configuration comprising a plurality of elongated annular cells, each cell having inner and outer annular electrodes with an electrolyte therebetween, said outer electrode and electrolyte being broken to contain an electrically conductive interconnect adjacent a selected segment of said inner electrode, said interconnect extending a selected axial length along each said cell, a first and a second cell positioned adjacent one another and electrically connected in series between the inner electrode of said first cell and the outer electrode of said second cell through said electrically conductive interconnect.

In preferred form, a fuel cell arrangement or cell stack is formed of a plurality of individual long annular cells of various cross-sectional shapes, each on the order of 30 cm. or more in length, and each joined electrically in series to the next through an at least one interconnection extending the full axial length of the cell. Each cell is formed of a long inner porous support

tube for structural integrity. Surrounding the tube periphery is a thin film porous electrode, preferably an air electrode or cathode. About the cathode is the solid electrolyte, which is in turn surrounded by the second porous electrode, preferably a fuel electrode or anode.

While the preferred inner cathode is a complete annular structure, the solid electrolyte and outer anode structures are discontinuous to provide space for an electrical interconnection for series contact between the cathode of one cell and the anode of the next cell. The interconnection on one side is contiguous with, or adjacent and otherwise electrically coupled to, a small radial segment of the inner cathode, generally along its entire axially active length. Bonded to the opposite side of the interconnection preferably is a contact segment of a porous electrode type material.

In this manner, each elongated tubular cell has a generally full length contact segment surface which can be readily placed electrically in series with an outer surface of a parallel cell. Preferably, the series connection is made through an elongated metal felt, metal strip or metallized inlay, disposed between two adjacent annular cells.

This arrangement provides a high reliability system since electrical connection is not merely through a large number of small current collecting conductors, but is made through an elongated surface spanning the active length of the tubular cell. Thus, localized failure will not defeat current transfer since the large portion of the contact surface which has not failed is still operational. Additionally, ohmic losses are small since the current is directed from one cell to the next through a short path which is normal to the annular surface. And, the disclosed arrangement needs only two main current collectors for any number of cells in series, one elongated axial collector at each end of the series of cells.

Another advantage of the elongated single cell concept is the ability for arranging cells electrically in series-parallel with, for example by cubic dense packing of tubes. The parallel connection is made through adjacent outer peripheries. This method of cell interconnection allows a multitude of interconnected cells in order to achieve any desired current and voltage combination.

The advantages, nature, and additional features of the invention will become more apparent from the following description of exemplary embodiments thereof when taken in connection with the accompanying drawings, in which:

Figure 1 is a schematic isometric view of a fuel cell system in accordance with a preferred embodiment of the invention;

Fig. 2 is an isometric section view of a singular tubular fuel cell;

Fig. 3 is a section view through two adjacent cells, particularly showing the interconnection between the cells;

Fig. 4 is an isometric schematic of another system configuration; and

Fig. 5 is a schematic section view of a series-parallel interconnection configuration.

Referring now to Fig. 1, there is shown a fuel cell arrangement 10, also herein referred to as a stack, comprised of a plurality of elongated annular fuel cells 12. Each fuel cell 12 is preferably tubular, and is electrically connected, in series, to an adjacent cell 12. Annular geometric configurations other than tubular are equally possible. This electrical connection is made along a selected axial length of the cells, preferably the entire electrochemically active length. Each cell 12 generates an open circuit voltage of approximately one volt, and hundreds of cells 12 can be connected in series in order to provide a desired system voltage. The stack energy can be usefully withdrawn through leads 14 and 16,

respectively electrically connected to current collecting bus bars 18 and 20. The two bus bars 18, 20 preferably extend, and are in contact with, the entire active length of the cells 12 at the ends of the stack.

Fig. 2 shows the preferred configuration for each annular fuel cell 12. The preferred configuration is based upon a system wherein a gaseous fuel, such as hydrogen or carbon monoxide, is directed axially over the outside of the cell 12, as indicated by the arrow 24, and an oxidant, such as air, indicated by the arrow 22, flows through the inside of the cell. It will be recognized that the location of the reactant fuel and oxidant can be interchanged such that air flows about the cells and fuel flows within the cells. This, however, requires the reversal of the cell electrodes, which is herein referred to as an inverted cell structure.

In preferred form, each cell 12 includes a porous support tube 26 which provides structural integrity to the cell. In an exemplary cell 12, the support tube is comprised of calcia stabilized zirconia forming a porous wall approximately one millimeter thick. Surrounding the outer periphery of the support tube 26 is a thin film porous air electrode, or cathode 28. The exemplary system cathode 28 is a composite oxide structure approximately 50-500 μm thick, which is deposited onto the support tube through well-known techniques. The cathode is, for example, comprised of doped and undoped oxides or mixtures of oxides in the perovskite family such as $LaMnO_3$, $CaMnO_3$, $LaNiO_3$, $LaCoO_3$, $LaCrO_3$, doped indium oxide, In_2O_3, and other electronically conducting mixed oxides generally composed of rare earth oxides mixed with oxides of cobalt, nickel, copper, iron, chromium and manganese, and combinations of such oxides.

Generally surrounding the outer periphery of the cathode 28 is a layer of gas-tight solid electrolyte 30, comprised of yttria stabilized zirconia approximately 20 to 50 μm thick, for the exemplary cell. The electrolyte

30 can also be deposited onto the cathode by well known techniques. However, a selected radial segment 32 of the cathode 28 is, for example, masked during fabrication, and an interconnect material 34 is deposited on the segment 32.

The interconnect material 34, which preferably extends the active length of each elongated cell 12, must be electrically conductive in both an oxidant and fuel environment. Accordingly, the exemplary cell includes a gas-tight interconnection 34 approximately the same thickness as the electrolyte, 20 to 50 μm. The preferred interconnection material is an oxide doped (Ca,Sr,M_g) lanthanum chromite film.

Substantially surrounding the solid electrolyte 30 is a second porous electrode, for example, a nickel-zirconia cermet anode 36. As shown, the anode 36 is also discontinuous, being spaced from the interconnection 34 a distance sufficient to avoid direct electrical communication between the anode 36 and both the interconnection 34 and the cathode 28. The exemplary anode 36 is about 50 μm thick.

Preferably, deposited over the interconnection 34 is a segment 38 which is preferably comprised of the same material as the anode 36, nickel or cobalt zirconia cermet, and of the same thickness, 50 μm.

Fig. 3 shows the series interconnection between consecutive fuel cells 12. The electrical interconnection is preferably enhanced by a metal felt 40, made, for example, of nickel fibers. The felt extends axially between the annular cells 12, and is bonded to each by pressure contact which causes sinter bonding during operation. In the inverted cell structure, where fuel flows inside of the cells, the felt material is made from conducting oxide fibers, such as doped In_2O_3 or others.

During operation, air flows through the center of the annular cells 12, and fuel passes over the exterior. Oxygen from air diffuses through the porous support

26 and cathode 28, and fuel diffuses through the anode 36. These process mediums electrochemically react through the electrolyte, generating products such as water vapor, carbon dioxide, heat and electrical energy. The high temperature water vapor and carbon dioxide are carried away from the cell with, for example, unburned fuel, and electrical power is transferred in series from the inner cathode 28 of one cell to the outer anode 36 of the next cell. The electrical power is usefully drawn through the leads 14, 16.

A variant of the cell structure is the circumferential segmentation of the elongated single cells as shown in Figure 4. This segmentation alleviates circulating currents within the electrodes which tend to result from simultaneous exposure to rich and depleted reactants over the electrode surface. Segmentation exposes each electrode area to reactants of generally similar concentration. Without segmentation, one end of the cell is exposed to generally fresh reactants, and the other to depleted reactants. Referring to Fig. 4, segment 44 is exposed to a richer reactant concentration than segments 46 and 48, when flow of both reactants is in the direction of arrows 50. The segmentation can be provided, for example, by masking selected portions 60 of the porous support tube 26 during fabrication, and depositing only a layer of electronically insulating solid electrolyte on the selected portions, in order to insulate the segments 44, 46, 48 and seal the otherwise porous portions.

An advantageous fuel cell system configuration which is provided by the elongated surface contact among adjacent annular cells is shown in Figure 5. The cells 12 are here positioned in a series-parallel electrical connection. For descriptive purposes, the arrangement includes rows 52 and columns 54. The cells of any given row 52', 52'', 52''' are electrically interconnected in parallel through the outer electrodes and metal felt 40'. Alternatively, the felt can be eliminated and the cells

positioned to abut one another along their axial length. Use of the felt is, however, preferred, in order to insure a large contact surface and avoid potential structural damage to the outer electrodes. Consecutive cells 12 along a column 54 are electrically interconnected in series, as shown in Figure 3, from the inner electrode of one cell to the outer electrode of the next cell. Thus, each cell in a row operates at substantially the same voltage, and voltage progressively changes among the cells of a column, typically varying by approximately one volt from cell-to-cell along a column. In this manner, any number of elongated cells can be interconnected to achieve a desired voltage and current output. Other configurations, in addition to the shown rectangular array, are equally possible.

The electrical power generated by the series-parallel interconnection is readily collected by only two plates 56, one in electrical contact with each cell of a row 52 at one extremity of the stack, and another in electrical contact with each cell of the row at the other extremity.

Since numerous changes may be made in the disclosed apparatus without departing from the spirit and scope thereof, it is intended that the material contained in the foregoing description and drawings by interpreted as illustrative, and not in a limiting sense.

What we claim is:

1. A high-temperature, solid electrolyte electrochemical cell configuration (10) comprising a plurality of elongated annular cells (12), each cell (12) having inner and outer annular electrodes (28, 36) with an electrolyte (30) therebetween, characterized in that said outer electrode (36) and electrolyte (30) are broken to contain an electrically conductive interconnect (34) adjacent a selected segment (32) of said inner electrode (28), said interconnect (34) extending a selected axial length along each said cell (12), a first and a second cell (12) positioned adjacent one another and electrically connected in series between the inner electrode (28) of said first cell and the outer electrode (36) of said second cell through said electrically conductive interconnect (34).

2. The electrochemical cell configuration of claim 1 further comprising a current collector (18) in electrical contact with the first of said cells (12) in series, along said selected axial length, and another current collector (20) in electrical contact with the last of said cells (12) in series along said selected axial length.

3. The electrochemical cell configuration of claim 1 wherein an electrically conductive insert (40) is provided between said first and second cells (12) and comprises a metal felt.

4. The electrochemical cell configuration of claim 1 wherein each said cell (12) includes a plurality

of segments (44, 46, 48), said segments of a cell (12) being electrically segmented from one another.

5. The electrochemical cell of claim 1, 2, 3 or 4 wherein said first and a third cell (12) are electrically connected to one another in parallel, from the outer electrode (36) of said first cell (12).

6. The electrochemical cell configuration of claim 5 further comprising a current collecting plate (56) in electrical contact with said first and third cells (12).

7. The electrochemical cell configuration of claim 5 or 6 wherein said adjacent cells (12) are arranged in rows and columns, the fuel cells (12) in each row (52) being electrically connected to one another in parallel, whereby each cell (12) in a row (52) operates at a similar voltage, and the fuel cells (12) in each column (54) being electrically connected in series to the fuel cells (12) in the next row along a column, whereby voltage changes from row to row along a column.

8. The electrochemical cell configuration of claim 7 wherein said rows (52) include a first row (52') and a last row (52'''), and further comprising a first current collecting plate (56) in electrical contact with each said fuel cell (12) of said first row and a second current collecting plate (56) in electrical contact with each said fuel cell (12) of said last row (52''').

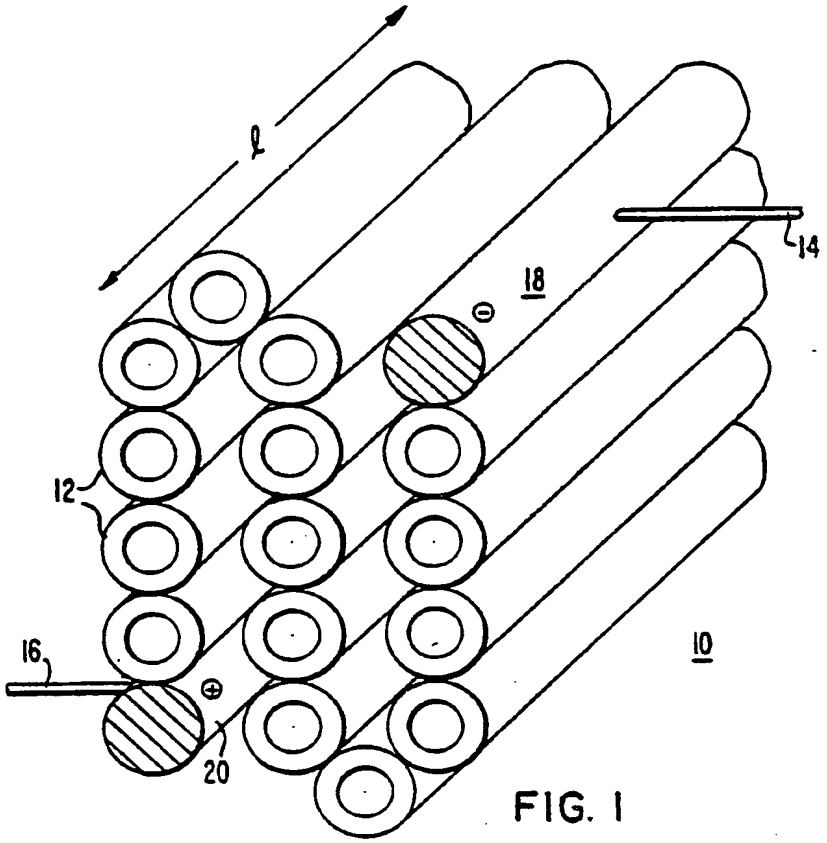


FIG. 1

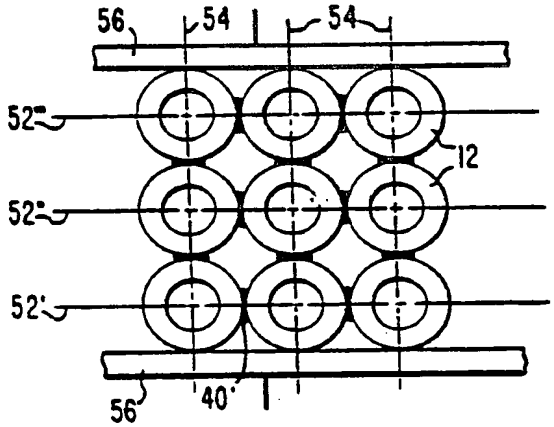
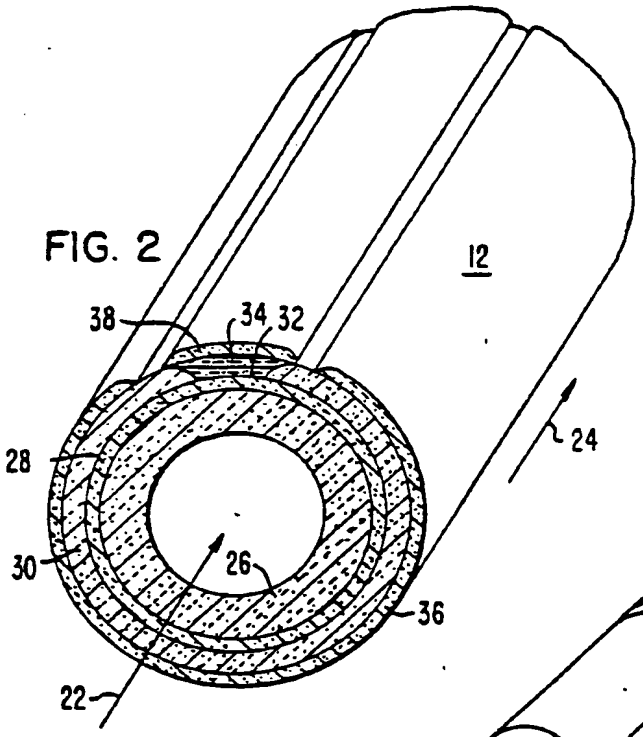


FIG. 5

FIG. 2



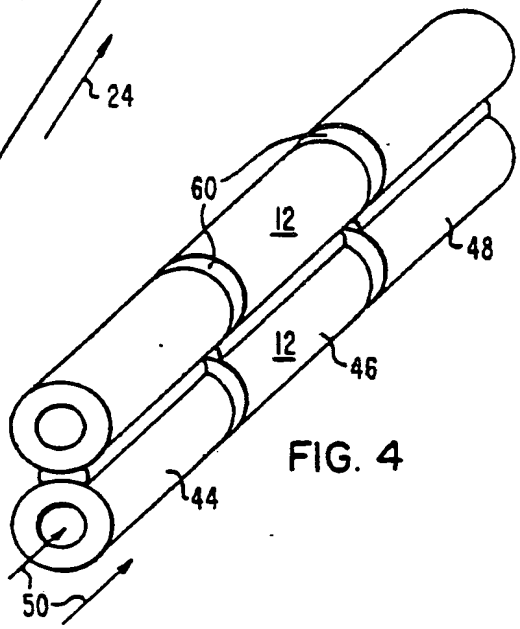


FIG. 4

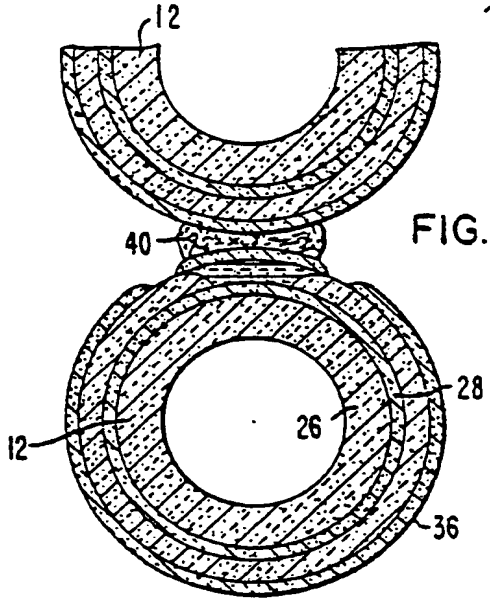


FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application number
0055016
EP 81305175.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - E - Re. 28 792 (RUKA et al.) * Fig. 6 * --	1
A	US - A - 4 204 033 (MEISSNER) (20-05-1980) * Fig. 3; column 4, lines 65,66 * ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

H 01 M 8/12
H 01 M 8/24
H 01 M 2/20

TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

H 01 M

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	25-03-1982	LUX

EPO Form 1503.1 06.78